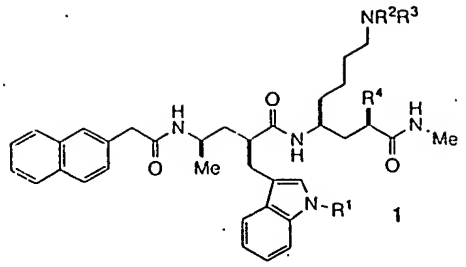
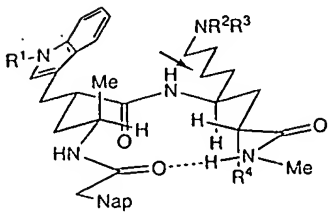
[16] We found that BRP-H is also a polymerization catalyst for other thiophenes, for example, 3-dodecyl-thiophene.
[17] *Handbook of Oligo- and Polythiophenes* (Ed.: D. Fichou), Wiley-VCH, Weinheim, 1999.
[18] D. Dini, F. Decker, F. Andreani, E. Salatelli, P. Hapiot, *Polymer* 2000, *41*, 6473.
[19] In the measurement setup an argon ion laser beam was focused by a 25 × microscope objective to a 50 μm diameter spot on the sample. The fluorescence emission was imaged by a 50 × objective on a CCD camera.
[20] No UV/Vis spectrum could be recorded from a single vesicle, nor from a suspension of vesicles, because of scattering problems.
[21] A 0.5 g L^{-1} solution of PS-PIAT dissolved in THF was injected into a 30 mg L^{-1} solution of CAL B enzymes; the final water/THF ratio was 12:1 (v/v). After the mixture was left for two days to equilibrate, it was dialyzed to dispose of all nonincluded enzymes.





Expected conformation of 1

1	R^1	R^2	R^3	R^4
a	Mes	Bn	Bn	H
b	Mes	Bn	Bn	Me
c	H	Bn	Bn	Me
d	Mes	Bn	H	Me
e	H	Bn	H	Me
f	Mes	H	H	H
g	H	H	H	H

Scheme 1. Structural formulae of the γ-peptides 1. In the expected conformation of 1 the red arrow points to a CH_2 group of the $H_2N(CH_2)_4$ unit, which is placed inside the shielding cone of the aromatic indole ring. Mes = mesitylenesulfonyl, Bn = benzyl, Nap = naphthyl.

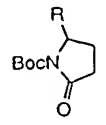
Somatostatin Mimics

Design and Synthesis of γ-Dipeptide Derivatives with Submicromolar Affinities for Human Somatostatin Receptors

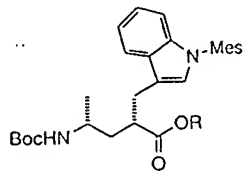
Dieter Seebach, Laurent Schaeffer, Meinrad Brenner, and Daniel Hoyer*

In a previous paper we have shown that simple *N*-acyl-γ-dipeptide amides that resemble a βII′ turn of an α-peptide can be designed to form a turn structure in solution (NMR) and in the solid state (X-ray).[1,2] To see whether such a turn could also be used to mimic a peptide, the biological activity of which rests upon a turn structure carrying functionalized side chains, we have now synthesized compounds **1a–g** (Scheme 1), with the side chain of tryptophan in the γ^2 position of the first and of lysine in the γ^4 position of the second γ-amino acid, and have tested their affinities for the human somatostatin receptors $hsst_{1-5}$.[3–6]

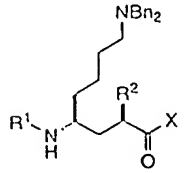
The synthesis of γ-dipeptide derivatives **1** commenced with the *N*-Boc-γ-lactams **2** and **3** (Boc = *tert*-butoxycarbonyl), readily available from the corresponding commercial (*R*)-Ala and (*S*)-Lys acids by known procedures.[1,7] Ring opening (with the Lys derivative after change of side-chain protection, →4), and esterification with $Me_3Si(CH_2)_2OH$ provided the (*R*)-Boc-γ^4-hhAla and Boc-γ^4-hhLys(Bn_2) esters, which were



(*R*)-**2**, R = Me
(*S*)-**3**, R = $(CH_2)_4NH$(2-Cl-Z)
(*S*)-**4**, R = $(CH_2)_4NBn_2$



5, R = $(CH_2)_2SiMe_3$
6, R = H



7, R^1 = Boc, R^2 = Me, X = $O(CH_2)_2SiMe_3$
8, R^1 = R^2 = H, X = NHMe
9, R^1 = H, R^2 = Me, X = NHMe

doubly deprotonated and alkylated with 1-mesitylenesulfonyl-3-bromomethylindole and MeI to give the *unlike* $\gamma^{2,4}$-amino acid derivatives **5** and **7**, respectively. The ester group in compound **5** with Trp side chain was cleaved (Bu_4NF, →6), and the lysine-derived esters were converted to the methylamides **8** and **9** without and with 2-methyl substitution, respectively (1. Bu_4NF, 2. $MeNH_2$, 3. F_3CCO_2H). Coupling of the two γ-amino acid derivatives (**6** + **8** and **6** + **9**), removal of the Boc groups, and acylation with 2-naphthylacetic acid[8] (4-methylmorpholine, 1-hydroxy-1*H*-benzotriazole, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) produced the side-chain-protected *N*-acyl-dipeptide amides **1a** and **1b**. Deprotection procedures ($MeSO_3H$, F_3CCO_2H, and Pd/C, H_2) led to the various partially or fully deprotected γ-dipeptide derivatives **1c–1g**. All compounds were purified and fully characterized by elemental analyses, specific optical rotations, circular dichroism (CD), IR, and NMR spectroscopy, and mass spectrometry.

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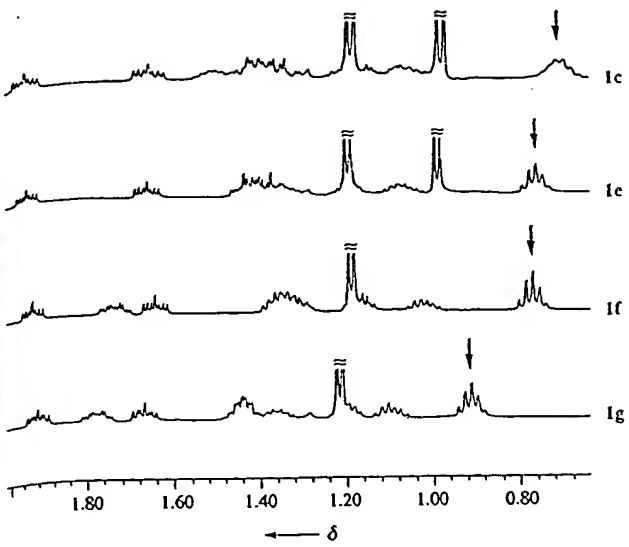

Figure 1. High-field part of the 500 MHz ^{1}H NMR spectra of the γ-dipeptides **1c**, **1e**, **1f**, and **1g** in CD_3OD. The red arrows point to high-field-shifted $N(CH_2)_4$ resonances.

A typical feature of the turn structure in somatostatin and its analogues is the juxtaposition of the tryptophan and lysine side chains, which places CH_2 groups of the $H_2N(CH_2)_4$ unit inside the shielding cone of the aromatic indole ring (NMR shifts between $\delta = 0.8$ and 0.3 ppm are observed).[9] High-field sections of the NMR spectra of four γ-dipeptide amides, shown in Figure 1, in which CH_2 signals appear between $\delta = 0.9$ and 0.6 ppm, confirm the proximity between the corresponding side chains, and are thus compatible with a turn conformation of these compounds. The CD spectra of the *N*-naphthylacetyl dipeptide amides **1** exhibit an intensive negative Cotton effect near 200 nm ([Θ] up to 70000 deg cm^2 dmol^{-1}), with a weaker and broader peak near 220 nm ([Θ] up to 30000 deg cm^2 dmol^{-1}) (Figure 2); this CD pattern may be taken as another piece of evidence for the presence of a secondary structure.

Probably the most stringent test of the γ-dipeptide structure is the affinity for somatostatin receptors. Binding affinities for the five cloned human receptors $hsst_{1-5}$, expressed in CCL-39 cell lines, were determined by displacement of [^{125}I]LTT-SRIF$_{28}$ from these receptor proteins.[10] While the fully protected γ-dipeptide **1d** binds to $hsst_1$ and $hsst_3$ with remarkable K_D values of 0.55 and 1.00 μM, respectively, the partially and the fully deprotected γ-dipeptide derivatives **1f** and **1g** bind to $hsst_5$ with K_D values of 0.51 and 0.87 μM, respectively (Table 1). Intriguingly, the highest affinities (**1d**/$hsst_1$, **1f**/$hsst_5$) are observed when the side chain functional groups (3-indolylmethyl and $(CH_2)_4NH_3^+$) are protected by bulky aromatic moieties (*N*-mesitylenesulfonyl and/or -benzyl)!

The results presented here are confirmative, surprising, and promising; they demonstrate that a 14-amino-acid cyclic disulfide hormone, somatostatin, can be mimicked by a simple, designed, low-molecular-weight, open-chain γ-dipeptide derivative (cf. **1g**) that contains only three amide bonds; they suggest that hitherto unknown hydrophobic pockets are present in the receptors ($hsst_1$, $hsst_3$, and $hsst_5$), which supposedly house the turn-bound Trp and Lys side chains (cf. **1c**, **1d**, **1f**); and they promise a potential of γ-peptides for the development of peptidase-resistant[11] peptidomimetic drugs.

Table 1: pK_D Values for γ-peptides **1b–1g** at the five hsst receptors expressed in CCL-39 cells and measured by radioligand binding assays with [^{125}I]LTT-SRIF$_{28}$ as radioligand.[a],[10]

Receptor	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	Octreotide[b]	SRIF$_{14}$[c]
$hsst_1$	5.47	6.06	6.26	5.61	5.98	4.73	6.45	9.08
$hsst_2$	<5	<5	5.17	<5	5.01	2.81	9.11	10.06
$hsst_3$	5.53	5.89	6.00	5.73	5.67	5.42	8.60	9.67
$hsst_4$	4.67	5.74	5.92	5.66	5.79	5.44	5.76	8.39
$hsst_5$	4.49	5.01	5.87	5.14	6.29	6.06	7.31	9.01

[a] Submicromolar affinities are highlighted in red. [b] Sandostatin. [c] Somatostatin.

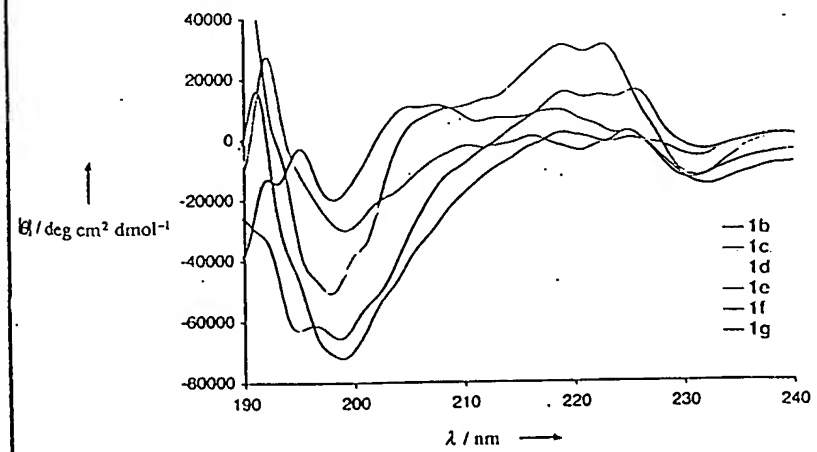

Figure 2. Nonnormalized CD spectra in MeOH (0.2 mM) of the γ-dipeptide derivatives **1b–1g**.

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Controlled Electropolymerization

Liquid-Crystal Templating of Conducting Polymers**

*James F. Hulvat and Samuel I. Stupp**

In organic electronics, conducting polymers have a number of advantages over small molecules, particularly because of their stability, mechanical properties, and ease of processing.[1,2] However, performance of some conducting polymers is limited by their high degree of disorder.[3,4] Molecular ordering improves carrier mobility in organic field-effect transistors and enhances charge injection in organic light-emitting diodes (OLEDs).[5] For this reason, vapor-sublimated crystalline films of small molecules are often used,[3] but alternative strategies to obtain molecular ordering would reduce cost and simplify fabrication of organic electronic devices. One possible way to achieve this is through molecular self-organization. Toward this goal we developed an aqueous, low-temperature technique for preparing conducting polymer films in a self-organized template.

Films of poly(3,4-ethyldioxythiophene) (PEDOT) are commonly used as hole injection layers in OLEDs. PEDOT can be polymerized in organic solvents or in an aqueous suspension with a soluble copolymer or surfactant, leading to amorphous films.[6] We have studied here the formation of PEDOT films by electropolymerization within a liquid crystalline template.

The well-known hexagonal (H1) lyotropic liquid crystal (LC) consists of cylindrical hydrophobic cores parallel to one another and separated by a hydrophilic continuum (see Figure 1 in the Supporting Information).[7] LCs have been used by us and others to template inorganic minerals as well as in the formation of mesoporous silica.[8] With regard to conducting polymers, template chemistry has been used to incorporate chains within the channels of mesoporous silica[9] or in aqueous channels of an inverse hexagonal LC.[10] These approaches, however, are limited to soluble, chemically polymerized polymers or to water-soluble monomers such as aniline or pyrrole. Our approach described here is novel in two key respects. First, polymerization occurs in the hydrophobic domain of the LC, allowing use of less polar

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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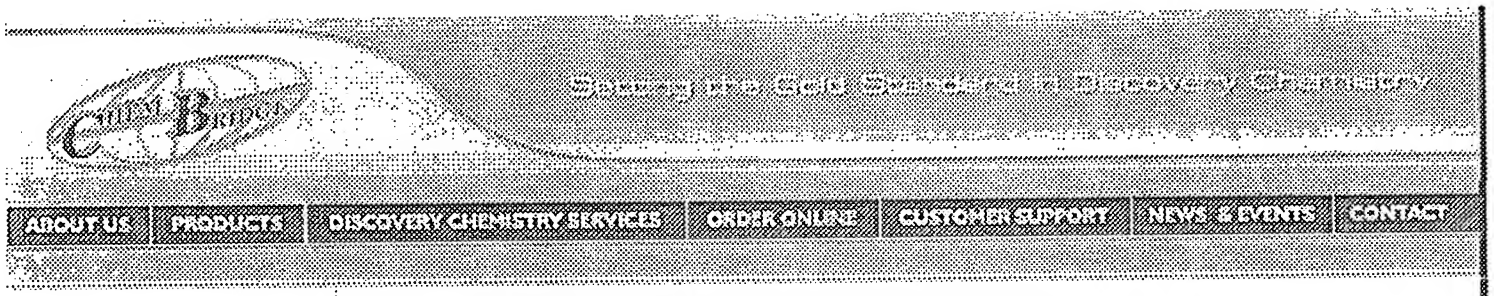

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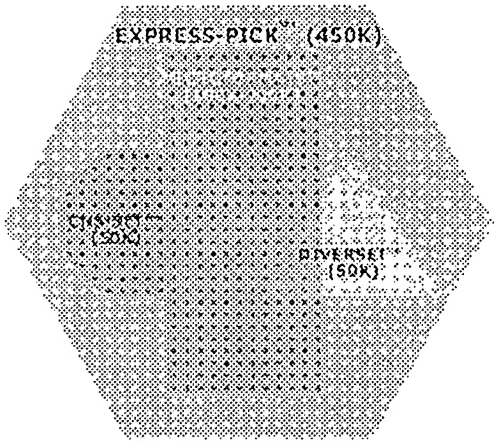

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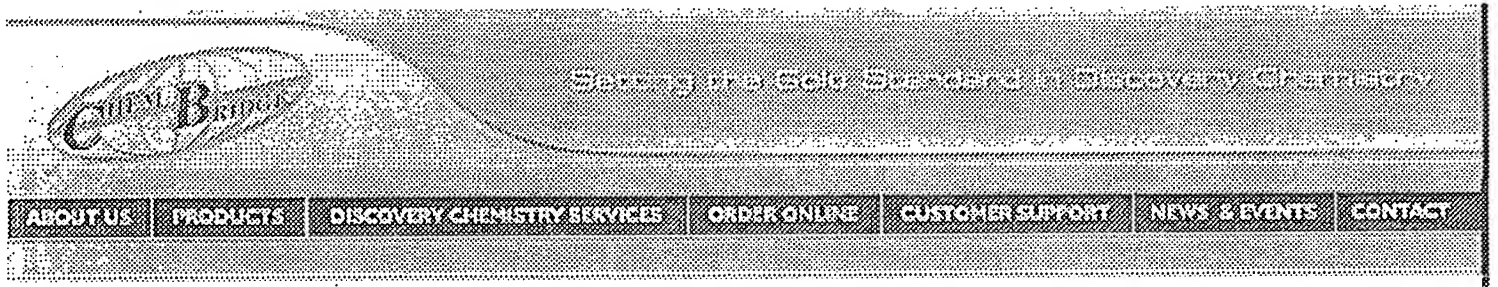

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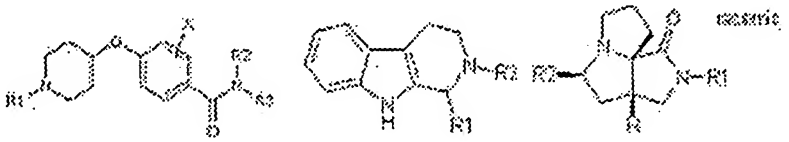

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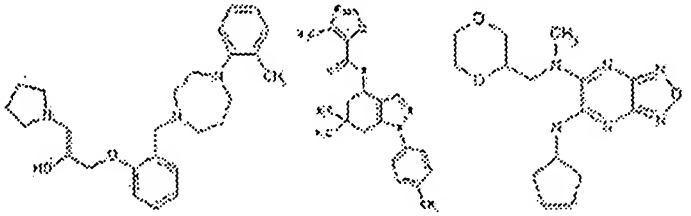

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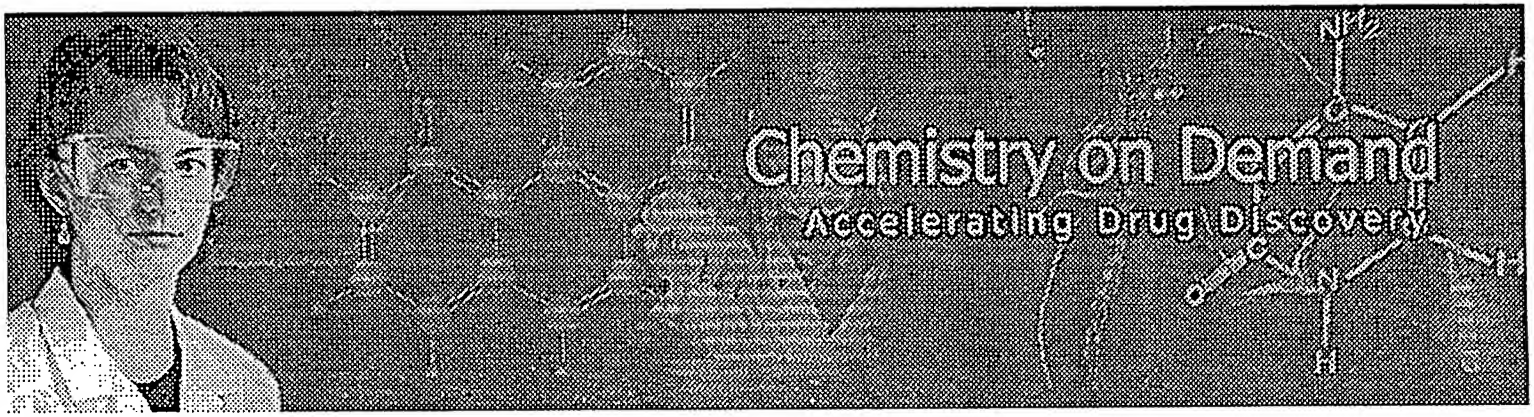
Click here for Physicochemical Properties

Specifications:

- Available in µmol amounts. Dry Film and/or mg formats may be considered upon request
- Samples can be ordered on a per plate basis; typically one template scheme per plate
- 100% QC with Purity > 80% by ^{1}H-NMR, actual data shows 50% of the samples are > 90% pure by ^{1}H-NMR
- CDA required to view structures

For more information, contact sales@chembridge.com.

NANOSYN



NANOSYN - Accelerating Drug Discovery

We are a chemistry-based company specializing in the design, synthesis and analysis of small organic compounds for the pharmaceutical and biotechnology industries. We place special emphases on custom synthesis, 'hit-to-lead' optimization, and the development of screening libraries targeted for drug discovery. Nanosyn's unique proprietary technology yields **PureQuality™** compounds enabling for the rapid identification of new drug candidates. .

Chemistry on Demand is the focal point of our platform which allows for the rapid production of chemical compounds as needed by a customer. Nanosyn's compounds and synthetic services are individually tailored to each and every requirement as specified by our customers. We don't suit your needs to our products; we suit our products to your needs.

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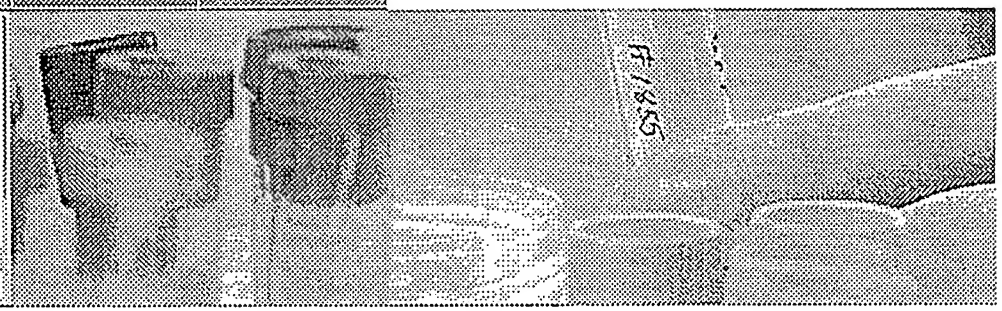
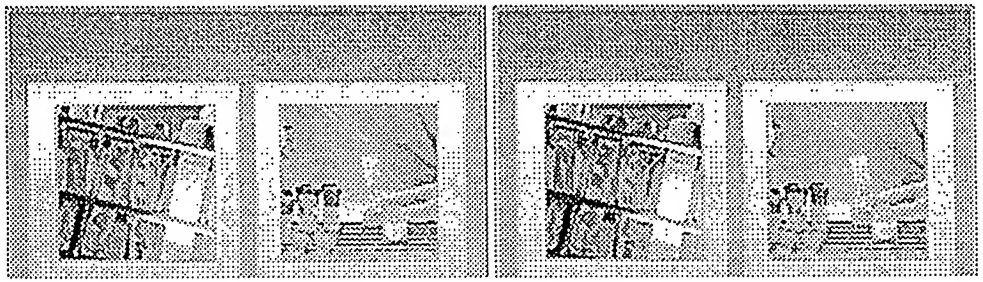
ActiMol
Compound collections



ActiMol Compounds and Compound Collections



ActiProbe-25 Collection

The ActiProbe-25 Collection is a pre-plated screening set of 25,000 compounds that has been assembled from molecules representative of the chemical diversity being produced by labs throughout the world.

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ActiProbe-10 Collection

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TimTec is introducing a new line of screening products based on rigorous structural fragment filtration and diversity selection that promise to improve the quality and efficiency of hit/lead identification and optimization.

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